Journal of Physics: Conference Series

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Journal of Physics: Conference Series **1389** (2019) 012129 doi:10.1088/1742-6596/1389/1/012129

Unusual weak increase of Curie temperature and lattice parameters in $Pr_2Fe_{16.5}Zr_{0.5}$

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Abstract. Crystal structure and magnetic and thermomagnetic properties of the $Pr_2Fe_{17-x}M_x$ compounds with M = Ti, V, Cr, Zr, Nb have been studied. The change of interatomic distances is not enough to explain the growth of the Curie point and it is necessary to assume the distribution of M = Ti, V, Cr, Nb atoms over the lattice positions, similar to that previously published for the $Nd_2Fe_{17-x}M_x$ compounds. It was established by neutron diffraction that Zr atoms substitute for Pr atoms in the 6*c* site and do not substitute for Fe atoms as might be expected from the original formula $Pr_2Fe_{16.5}Zr_{0.5}$. So, the real composition of the substituted compound studied is $Pr_{1.48(8)}Zr_{0.52(8)}Fe_{17}$. The magnetic moment of Fe atom and the magnetocaloric effect in the $Pr_2Fe_{17-x}M_x$ compounds decrease with decreasing Fe content.

1. Introduction

Magnetic refrigeration based on the magnetocaloric effect (MCE) is currently a topic of growing interest due to high efficiency, reliability, and environmental safety. A large MCE is often intrinsic to materials with large values of the magnetic moment. The best materials for the refrigeration purpose are ferromagnets or antiferromagnets. The R_2Fe_{17} intermetallic compounds, where R represents a rare earth element, have become promising as magnetocaloric materials due to their large magnetization, magnetic ordering temperature close to room temperature, low cost of their principal component, easy fabrication, and the absence of magnetic hysteresis. The MCE in the R_2Fe_{17} binaries is moderate [1], but it can be increased by varying composition [2]. Therefore, it is interesting to study magnetic, structural and magnetothermal properties of the partial substituted $Pr_2Fe_{17-x}M_x$ compounds, M = Ti, V, Cr, Zr, Nb. The Pr_2Fe_{17} and Nd_2Fe_{17} compounds have the highest magnetic moment and unit cell volume among the R_2Fe_{17} intermetallic compounds with magnetic R. They crystallize in the rhombohedral Th_2Zn_{17}-type structure in which Fe atoms occupy four various positions 9*d*, 18*f*, 18*h* and 6*c*, R atoms occupy 6*c* position. However, the substituted alloys based on Pr_2Fe_{17} are much less studied as compared to $Nd_2Fe_{17-x}M_x$ [3-5].

2. Experimental details

The $Pr_2Fe_{17-x}M_x$, x=0, 0.5, 1, M=Cr, V, Ti, Nb, Zr compounds were prepared by induction melting. The ingots were homogenized at 1293 K for 14 days and then quenched in water. X-ray powder diffraction analysis was employed to determine the phase composition, structure type and lattice parameters under ambient conditions. A diffractometer of Empyrean Series 2 (PANalytical) and CuKα radiation were used. The HighScore v.4.x programs were used for calculation of the lattice parameters

and analysis of phase compositions. The site distribution of Zr in the $Pr_2Fe_{16.5}Zr_{0.5}$ compound was studied by means of the Fourier-diffractometer of high resolution FDHR on the fast pulse IBR-2 reactor in LNP JINR. The refinement of the structure parameters (coordinates, occupancies, unit-cell dimensions, etc.) of $Pr_2Fe_{16.5}Zr_{0.5}$ was performed using the full-profile Rietveld analysis with the "FULLPROF" program. MPMS and 7407 VSM (Lake Shore Cryotronics) devices were used for magnetic study. The saturation magnetization M_{sat} at 4 K was determined by the linear extrapolation of the high-field part of the *M(H)* curves measured on free powder samples to zero inverse internal field (1/*H*). The temperatures of the magnetic phase transitions were determined from the ac susceptibility vs. temperature curves. The magnetization isotherms *M(H)* were recorded on polycrystalline spherical samples in a magnetic field of strength up to 1.7 T.

3. Experimental results and discussion

3.1. Crystal structure analysis

The compounds investigated crystallize into the rhombohedral Th_2Zn_{17}-type structure. The fraction of free α-Fe in $Pr_2Fe_{16.5}M_{0.5}$ being no larger than 3 wt.%. The $Pr_2Fe_{16}M$ compounds contain no larger than 4 wt.% of MFe_2, besides $Pr_2Fe_{16}Nb_1$ with about 7 wt.%. of $NbFe_2$. The solubility of M in Pr_2Fe_{17} decreases in the following sequence as atomic radius *r* increases: Fe (*r* = 1.274 Å), V (1.346 Å), Cr (1.360 Å), Ti (1.462 Å), Nb (1.468), Zr (1.602 Å). Respectively, one can see from Fig. 1 that partial substitution of Fe by larger Nb or Ti atoms leads to the maximal increase of the unit cell volume *V*. At the same time, *V* unexpectedly decreases in the case of Cr and is almost the same with Zr, although Cr atom is larger and Zr atom is much larger than Fe atom.

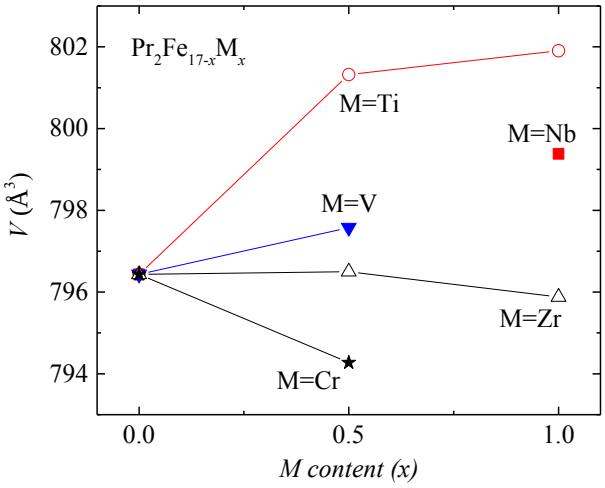

Figure 1. Concentration dependence of the unit-cell volume *V* of the $Pr_2Fe_{17-x}M_x$ compounds.

3.2. Magnetic properties

The Curie temperature T_C of $Pr_2Fe_{17-x}M_x$ increases for all M as is shown in Fig. 2. It is commonly assumed that T_C of the rare-earth R_2Fe_{17} compounds is determined by the competition of positive and negative exchange interactions between Fe atoms. The negative Fe-Fe exchange interaction dominates when the distance between the Fe atoms is lower than the critical one equaled to 2.45 Å. In the so-called "dumbbell" position 6*c*, two Fe atoms are oriented along the *c*-axis of the crystal and the Fe-Fe distance is minimal. However, T_C of $Pr_2Fe_{16.5}Ti_{0.5}$ and $Pr_2Fe_{16.5}Cr_{0.5}$ are the same (Fig. 2), although their *V* increases and decreases in comparison with *V* for Pr_2Fe_{17}, respectively. Apparently, in this case the preferential substitution of Fe atoms by M atoms in the 6*c* site plays the decisive role in T_C increasing, as it is in the case of the $Nd_2Fe_{17-x}M_x$ compounds [3-5].

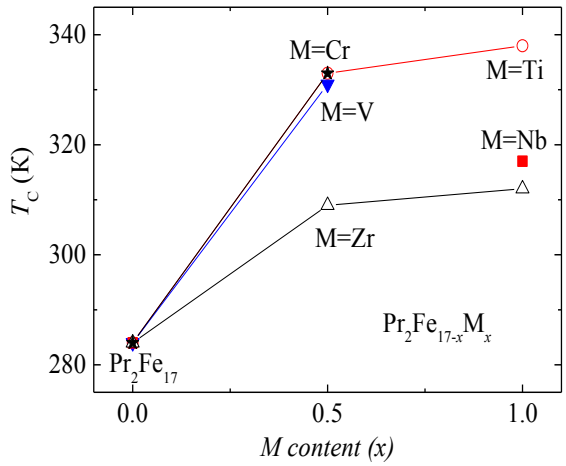

Figure 2. Concentration dependence of the Curie temperature T_C of the $Pr_2Fe_{17-x}M_x$ compounds.

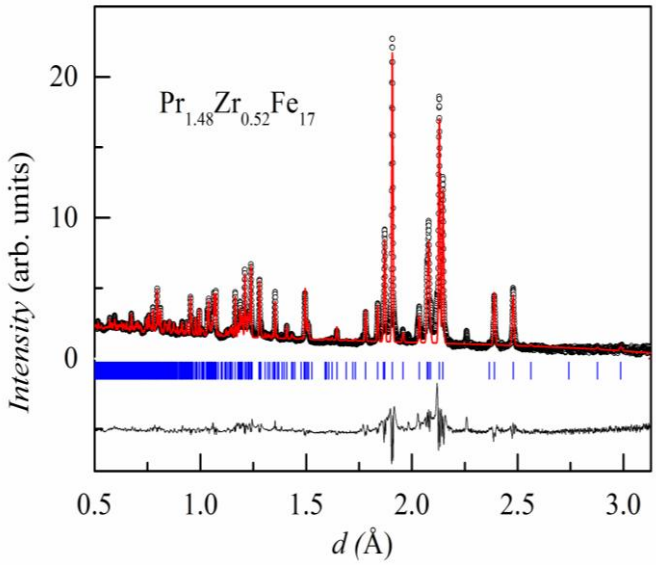

Figure 3. Neutron diffraction pattern of the $Pr_{1.48}Zr_{0.52}Fe_{17}$ compound (circles) and its fitting (envelop curve). The lower curve is the difference between the experimental and the calculated results. The vertical lines show the reflection positions for the Th_2Zn_{17}-type lattice.

The increases of the Curie temperature ΔT_C and the unit-cell volume ΔV are minimal in the case of Zr atoms (ΔT_C = 25 K, ΔV = 0.54 Å^3) in comparison with the much smaller atoms of Cr (ΔT_C = 49 K, ΔV =-0.46 Å^3), V (45 K, 1.74 Å^3) or Ti (49 K, 4.24 Å^3). Neutron diffraction was used to study this phenomenon. The results of the structural investigation of the Pr_2Fe_{17} and $Pr_2Fe_{16.5}Zr_{0.5}$ compounds are presented in Fig. 3 and in Tables 1 and 2. It was established that Zr atoms (r =1.602 Å) substitute for Pr atoms (r =1.828 Å) in the 6*c* site and do not substitute for Fe atoms as it was suggested by the original formula $Pr_2Fe_{16.5}Zr_{0.5}$ of the alloy (Table 1). So, the real composition of the studied alloy is $Pr_{1.48(8)}Zr_{0.52(8)}Fe_{17}$. The distances D between neighboring Fe atoms in the Pr_2Fe_{17} and $Pr_{1.48}Zr_{0.52}Fe_{17}$ compounds are presented in Table 2. One can see that the D values are about the same in both compounds. This fact explains the almost unchanged unit-cell volume when doping Zr. As a result, the increase of T_C in the $Pr_2Fe_{17-x}M_x$ system is minimal for Zr although its atomic radius is maximal among M. Our results differ from those obtained earlier for the $Nd_2Fe_{17-x}Zr_x$ system in Ref. [3], in which

neutron diffraction study showed that Zr atoms replace Fe atoms in the positions 18*f* (predominantly) and 6*c*.

Table 1. Structural parameters of $Pr_{2-x}Zr_xFe_{17}$. The Th_2Zn_{17}-type structure (space group R-3*m*): Pr/Zr(6*c*) (0, 0, *z*), Fe(6*c*) (0, 0, *z*), Fe(9*d*) (1/2, 0, 1/2), Fe(18*f*) (*x*, 0, 0) and 18*h* (*x, -x, z*).

***x* (Zr)**		0	0.52
***a*, Å**		8.5820(2)	8.5864(1)
***c*, Å**		12.4629(3)	12.4770(23)
***V*, Å^3**		794.94(3)	796.65 (2)
Pr(6*c*)	***z***	0.3450(5)	0.3421(5)
	***B*, Å^2**	0.81(7)	1.25(9)
	occ.	2.0	1.48(8)
Zr(6*c*)	***z***	0.3450(5)	0.3421(5)
	***B*, Å^2**	0.81(7)	1.25(9)
	occ.	0	0.52(8)
Fe(6*c*)	***z***	0.0968(2)	0.0950(2)
	occ.	2.0	2.0
Fe(9*d*)	***occ.***	3.0	3.0
Fe(18*f*)	***x***	0.2877(1)	0.2896(1)
	occ.	6.0	6.0
Fe(18*h*)	***x***	0.1688(1)	0.1694(1)
	z	0.4897(1)	0.4884(1)
	occ.	6.0	6.0
Fe (total)	***B*, Å^2**	0.50(1)	0.68(1)

Table 2. The distances D between neighboring Fe atoms in the $Pr_{2-x}Zr_xFe_{17}$ compounds as obtained from the neutron diffraction data.

Fe-Fe sites	6*c*-6*c*	6*c*-9*d*	6*c*-18*f*	6*c*-18*h*	9*d*-18*f*	9*d*-18*h*	18*f*-18*f*	18*f*-18*h*	18*f*-18*h*	18*h*-18*h*
***D*, Å (*x*=0)**	2.41	2.63	2.75	2.64	2.44	2.46	2.47	2.54	2.67	2.52
***D*, Å (*x*=0.52)**	2.37	2.64	2.75	2.65	2.44	2.46	2.49	2.56	2.65	2.54

Magnetic moment M_{Fe} of a Fe atom in $Pr_2Fe_{17-x}M_x$ decreases as M content increases, for example, M_{Fe} = 2.02 μ_B for x=0 and M_{Fe} = 1.69 μ_B for x=1 in $Pr_2Fe_{17-x}Ti_x$. This effect can be explained by increase of the direct hybridization between *d*-electrons of Fe and M atoms.

The isothermal magnetic entropy change $-\Delta S_M$ (i.e. the magnetocaloric effect MCE) was calculated from the magnetization isotherms $M(H)$ using the well-known Maxwell relation [1,2]. The MCE

decreases monotonically in the $Pr_2Fe_{17-x}M_x$ system as x increases and takes about the same values for all M: $-\Delta S_M$ = 2.9 J/kg*K for x=0 and $-\Delta S_M$ = 1.9 J/kg*K for x=1 in a field of $\mu_0 H$ = 1.7 T. Apparently, this decrease of MCE is due to the monotonic decrease of the spontaneous magnetization of the alloys during doping.

4. Conclusion

Substitution of Fe atoms in Pr_2Fe_{17} by larger atoms M = V, Cr, Ti, Nb, Zr does not always results in a proportional increase in volume of the unit cell V and Curie temperature T_C. Apparently, this is caused by the different character of the preferred replacement of Fe atoms by M atoms among crystallographic positions. By means of neutron diffraction, it was established that Zr atoms substitute for Pr atoms and do not substitute for Fe atoms as it was suggested by the original formula $Pr_2Fe_{16.5}Zr_{0.5}$. Therefore, the lattice parameters, interatomic distances Fe-Fe and T_C of the substituted alloy change insignificantly, although the Zr atomic radius is the largest among M. The magnetic moment of the Fe atom and the magnetocaloric effect of the $Pr_2Fe_{17-x}M_x$ compounds decrease with increasing concentration of the alloying metal.

Acknowledgments

The research was carried out within the state assignment of Minobrnauki of Russia (themes “Magnet” No. AAAA-A18-118020290129-5, “Alloys” and “Flux” No. AAAA-A18-118020190112-8) and supported in part by RFBR (project No. 18-02-00294).

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